Journal of Scientific & Industrial Research
Vol. 63, August 2004, pp 677-681

Studies on nickel hydrazinium nitrate (NHN) and bis-(5-nitro-2H tetrazolato-N^2)tetraamino cobalt(III) perchlorate (BNCP): Potential lead-free advanced primary explosives

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Received 09 January 2004; accepted 22 April 2004

Nickel hydrazinium nitrate (NHN) and bis-(5-nitro-2H tetrazolato-N^2) tetraamino cobalt perchlorate (BNCP) have been synthesized and characterized. The performance evaluation of NHN in detonator tube No. 27 indicates that NHN offers a relatively safe alternative to lead styphnate as well as part replacement of lead azide. However, BNCP could be initiated only in the presence of high impulse flash donor compounds such as cobalt *tris*-(carbohydrazide) perchlorate(CCP)/nickel tris-(carbohydrazide) perchlorate (NCP) despite its high velocity of detonation. The results obtained in terms of extent of damage to witness plate are compared with the standard detonator No. 27 containing ASA (azide, styphynate and aluminium) composition. Also reports the studies on initiation of RDX/TNT (700/300 g) demolition charge by NHN: CE (350/500/900:550/400/0 mg) and NCP:BNCP:CE (50:300:550 mg) filled in detonator tube No. 10.

Keywords: Nickel hydrazinium nitrate, Explosives, Cobalt (III) perchlorate, Lead-free explosives

IPC Code: **Int. Cl.^{7}** : F 2 B 4/30

1 Introduction

During the past eight decades the most prominent primary explosives which found application in military devices are mercury fulminate (MF), lead azide (LA), silver azide (SA), lead styphnate (LS), and tetrazene. Currently, inorganic azides namely LA and SA are being widely used as key components of detonant composition. The tubular detonators like, detonator No. 27, normally contains a mixture of service LA, LS, and Al powder popularly known as ASA composition. Lead azide the main primary explosive has considerable advantage in terms of detonative potential. However, it is beset with the problems of high sensitivity due to typical structural features. Further, hydrolysis of lead azide leads to the formation of hazardous hydrazoic acid, which on reaction with copper in the encapsulating casing may form highly sensitive copper azide leading to eventuality of serious accidents. Lead itself increases toxicity and contamination. This has led to intensified R & D work in ordnance community to develop lead-free initiatory compounds, which can overcome the limitations of the conventional initiator. Silver azide is being explored for specific initiator applications[1-3]. It possesses a favorable combination of high chemical stability and initiating power[1]. However, it is more sensitive to friction stimuli than even lead azide.

These limitations of current initiator compositions have intensified research efforts towards lead and azide free safe energetic primary explosives based on co-ordination compounds[4] having almost stoichiometric fuel and oxidizer fractions within the molecule. In view of the desired physicochemical characteristics, nitrate/perchlorate complexes[6] of transition metals have emerged as preferred choice with energetic heterocyclic compounds based on nitro tetrazoles and triazoles ligands[7]. Carbohydrazide is another interesting key ligand, which has evinced interest in the synthesis of co-ordination compounds[8,9]. Synthesis, characterization, and thermodynamics of coordination compounds of metal nitrates and perchlorates with carbohydrazide have been reported by various researchers.[10-13] Bis-(5-nitrotetrazoleto-N^2)-tetraamine cobalt perchlorate (BNCP) has found application as energy producing component for semi-conducting bridge (SCB) initiator application[3]. Authors have recently reported the synthesis and characterization of NHN[14,15]. The work carried out on the synthesis and characterization of CCP and NCP has been reported earlier[16]. In continuation[14,] of our work on energetic co-ordination compounds for practical application, this paper presents detailed studies on the performance evaluation of NHN and BNCP as safe detonants. The energetic co-ordination compounds such as, nickel tris-(carbohydrazide) perchlorate (NCP) and cobalt tris-(carbohydrazide) perchlorate (CCP) have also been used as co-initiators of BNCP in the present study.

2 Experimental Procedure

2.1 Materials

Materials such as, nickel nitrate, hydrazine hydrate, cobalt/nickel perchlorate, carbohydrazide, and amino tetrazole were of AR grade and used as such.

2.2 Synthesis of NHN and BNCP

NHN was synthesized by the addition of aqueous solution of hydrazine hydrate to the solution of nickel nitrate at 65°C by the method reported earlier.[14] BNCP was obtained[15] by condensing sodium salt of nitrotetrazole with carbonato tetraamino cobalt (III) acetate (CTCA). The synthesized materials were characterized by metal content analysis, FT-IR, and DTA studies. The determined explosive properties such as, impact and friction sensitivities compared to the reported data[14,15].

The freshly prepared CCP, NCP, LA (azide content > 95 per cent) and SA used in the performance evaluation of NHN and BNCP also were synthesized by reported[1, 16] methods.

2.3 Performance Evaluation

2.3.1 Flash Sensitivity of NHN

NHN/BNCP (350 mg) was filled into the stem of tubular detonator No. 27 and pressed at 30 MPa with dwell time of 45 s. Safety fuse having 20 cm length was inserted into the tubular detonator touching the filled NHN/BNCP layer and crimped softly. Relative humidity (R_H < 55 per cent) was ensured in the process room throughout the filling operation. For evaluation the NHN filled tubular detonator was vertically held on 3 mm lead plate and the safety fuse was initiated by flame match. Damage to the lead plate, if any, was measured in terms of the diam of the neatly punched hole.

2.3.2 Hot Wire Sensitivity

Sensitivity of NHN /BNCP to hot wire was also tested by pressing the compound over a plug (squib) soldered with a bridge wire (Nichrome) connected to an electrical circuit.

2.3.3 Determination of Velocity of Detonation (VOD) of NHN and BNCP

The velocities of detonation of NHN and BNCP were determined by flash X-ray radiographic technique as per the standard procedure.

2.3.4 Effect of Consolidation Pressure on the Functioning of NHN

To assess the effect of consolidation of NHN, 100 mg of compound was pressed in the increments of 50 mg at 10-150 MPa with a dwell time of 45 s in the detonator (No. 27) tube to achieve uniform loading density. The filled samples were tested as per procedure mentioned under 2.3.1.

2.3.5 Performance Evaluation

NHN/BNCP (150 mg) was filled into tubular detonator and pressed at optimum (30 MPa) pressure with dwell time of 45 s. Lead azide/silver azide (200 mg) was pressed above the NHN at 10 MPa under identical conditions and performance was evaluated in terms of damage to witness plate. Similarly, series of experiments were carried out by increasing the quantity of NHN /BNCP simultaneously by reducing the quantity of LA/SA in the increment of 25 mg

In the further experiments, secondary explosive tetryl/pentaerthritol (PETN, 550 mg) was filled into tubular detonator No. 27 and pressed at 10 MPa with dwell time of 45 s. NHN was then introduced and pressed at 30 MPa. Lead azide/silver azide in optimized proportion of NHN was pressed above the tetryl/PETN and NHN at 10 MPa under identical conditions. The safety fuse having 20 cm length was inserted into the filled tubular detonator touching the layer of NHN and crimped softly and was evaluated similarly.

As BNCP, could not be initiated, under similar set of experiments, further studies were undertaken on its combination with NHN/CCP/NCP. In these sets of experiments, BNCP (300 mg) was filled in to the stem of detonator No. 27 and CCP/NCP (50 mg) and pressed above the BNCP layer following the above procedure and evaluated. The combination was decided after optimization studies as in the case of NHN and lead azide system. The selected combination was also evaluated along with tetryl in detonator tube No. 27, using fuse wire initiation.

The standard detonator No. 27, containing service lead azide (SLA, 65 per cent), lead styphnate (LS, 32.5 per cent) and Al (2.5 per cent) pressed above the initially pressed base charge of high explosives

CE/PETN/RDX was used as reference.

2.3.6 Detonator Filling in Detonator No.10

In order to evaluate potential of detonator as initiator in demolition devices, NHN and BNCP were also evaluated in detonator tube No. 10. CE base charge (550/400 mg) was pressed at 10 MPa and NHN (350/500 mg) was pressed at 30 MPa in the stem of detonator No. 10, with dwell time of 45 s. The explosive train comprised NHN filled detonator, perforated booster (95/5 RDX/Wax) pellet and RDX/TNT (60/40) charge. The train was initiated by safety fuse as well as LFCN based general purpose squib. The functioning of the explosive train was established by observing a puncture on 10 mm thick mild steel witness plate. NHN (900 mg) alone was also filled and pressed at 30 MPa in detonator tube No. 10 and evaluated, as done earlier. For BNCP (300 mg), similar sets of experiments were carried out in combination with CCP/NCP (50) along with tetryl (550 mg).

3 Results and Discussion

The bulk density of the synthesized and characterized (Table 1) NHN and BNCP was increased to 1.2 g/cm^3, and 0.6 g/cm^3, respectively, by the addition of additives like 1 per cent dextrin and dioctyl succinate, during the synthesis process.

The tests conducted during present study established that NHN responds to initiation by flash and hot wire stimuli. However, BNCP, under these test conditions could not be initiated by these stimuli. The combination of BNCP with NHN also could not be initiated. However, BNCP in combination with co-initiators such as, CCP/NCP could be initiated by flash as well as hot wire stimuli.

Experimentally determined velocities of detonation (by flash X-ray technique) for NHN and BNCP were 3600 and 5700 m/s at tapping density of 0.8 and 0.3 g/cm^3, respectively. However, VOD of NHN could be increased up to 6900 m/s by consolidation under pressure up to 150 MPa resulting in high loading density of 1.7 g/cm^3. VOD obtained, is in close agreement with the reported results[13].

NHN (350 mg) filled and pressed up to 30 MPa in detonator No. 27 did not produce discernable effect on witness plate. The results obtained establish that NHN need to get consolidated at 30 MPa to produce shockwave and it does not get dead pressed at higher pressures unlike mercury fulminate.

As NHN contains metal and fuel moieties, in combination with oxidant, it is expected to undergo combustion producing flash. Considering these aspects, lead styphnate was replaced by NHN in initial performance trials conducted in detonator No. 27. Subsequently, lead azide was replaced by NHN in the increments of 25 mg. It was consolidated at 30 MPa, considering the safety aspects in view of the presence of secondary explosives in detonators as booster charge. Combinations of NHN (25 to 325 mg) and LA (325 to 25 mg) damaged the witness plate (punched the hole diam of 9 mm) on par with the standard ASA composition. However, NHN alone (350 mg) filled in the detonator tube did not puncture the hole on the witness plate. In view of these findings, optimized combination (NHN 325 mg: LA 25 mg) was selected for evaluation in combination with tetryl /PETN (550 mg) pressed in the stem of detonator No. 27. It produced punched hole of 9 mm diam on witness plate, equivalent to that in the case for standard detonator No. 27, establishing that this combination produces wave capable to travel through the booster charge and initiate the latter (Table 2).

The detonators filled with BNCP in similar combinations with LA/NHN (50 mg) did not produce discernible effect on the witness plate like BNCP alone. However the BNCP (300mg) along with

Table 1 — Characterization data of NHN[14] and BNCP[15]

Sl No.	Characteristic properties	NHN	BNCP
1	Metal content (per cent)	20.6 (20.3)	12.96 (12.49)
2	Crystal morphology	Pink – square Shape	Light orange needle shape
3	Bulk density g/cm^3 (Without any additives)	0.85-0.90	0.3
4	Impact sensitivity Ht. 50 per cent explosion (cm) , with 2 kg wt.	96	30
5	Friction insensitiveness (kg)	1.0	3.0
6	Spark insensitiveness (j)	~5	~5
7	Explosion temperature (°C)	219	260
8	Energy of activation (k J/mole)	80	135

The values given in bracket are theoretical metal content values

Table 2 — Performance evaluation of NHN in detonator No. 27

Experiment No.	Composition Quantity given mg in bracket	Puncture on witness plate* Dia of the hole (mm)	Remarks
1	NHN (150) + LA/SA (200)	9	Initiated
2	NHN (175) + LA/SA (175)	9	Initiated
3	NHN (200) + LA/SA (150)	9	Initiated
4	NHN (225) + LA/SA (125)	9	Initiated
5	NHN (250) + LA/SA (100)	9	Initiated
6	NHN (275) + LA/SA (75)	9	Initiated
7	NHN (300) + LA/SA (50)	9	Initiated
8	NHN (325) + LA/SA (25)	9	Initiated
9	NHN(350)	No puncture	Dent on witness plate
10	NHN (325), LA(25) and tetryl /PETN (550)	9	Initiation
11	ASA Composition (Standard)	9	Initiated

NHN: Nickel hydrazinium nitrate, LA : Lead azide, SA : Silver azide; PETN: Pentaerthritol
ASA composition: Service lead azide (SLA, 65 per cent), Lead styphnate (LS, 32.5 per cent) and Al (2.5 per cent)
*Each experiment was repeated 5 times in order to prove the reproducibility in detonator No. 27

Table 3 — Performance evaluation of BNCP in detonator No. 27

Experiment No.	Composition quantity given mg in bracket	Puncture on witness plate* Dia of the hole (mm)	Remarks
1	BNCP (150) + LA (200)	No Puncture	No initiation
2	BNCP (150) + NHN(200)	No Puncture	No initiation
3	BNCP (150) + NCP/CCP (200)	9	Initiated
4	BNCP (175) + NCP/CCP (175)	9	Initiated
5	BNCP (200) + NCP/CCP (150)	9	Initiated
6	BNCP (225) + NCP/CCP (125)	9	Initiated
7	BNCP (250) + NCP/CCP (100)	9	Initiated
8	BNCP (275) + NCP/CCP (75)	9	Initiated
9	BNCP (300) + NCP/CCP (50)	9	Initiated
10	BNCP (325) + NCP/CCP (25)	6	Initiated
11	NCP/CCP (350)	9	Initiated
12	BNCP (325), NCP (25) and tetryl /PETN (550)	9	Initiated
13	BNCP (150), NCP (200) and tetryl /PETN (550)	9	Initiated
14	ASA Composition (Standard)	9	Initiated

BNCP: Bis-(5-nitro-2H tetrazolato-N^2)tetraamino cobalt(III) perchlorate LA : Lead azide; SA : Silver azide; PETN: Pentaerthritol CCP: cobalt carbohydrazide perchlorate NCP: Nickel carbohydrazide perchlorate
ASA composition: Service lead azide (SLA, 65 per cent), Lead styphnate (LS, 32.5 per cent) and Al (2.5 per cent)
* Each experiment was repeated five times to prove the reproducibility in detonator No. 27

NCP/CCP (50 mg) as well as in combination with tetryl (550 mg) produced 5-6 mm hole on witness plate, which was relatively less in comparison to standard ASA composition as well as LA/NHN combination with tetryl, suggesting formation of medium power detonation wave (Table 3).

Interestingly, NHN (350 /500/900) pressed at 30 MPa in the stem of detonator No. 10 along with CE (550/400/0 mg) on initiation by safety fuse and electrical squibs detonated RDX/TNT main demolition charge (700 and 300 g charge weight) placed over a steel witness plate of 6 mm thickness without the necessity of combining it with LA. Even NHN alone (900 mg) was found effective in this regard. This may be an outcome of built up of high pressure due to higher strength of material of construction of the detonator tube No. 10 than that of detonator No. 27 (Table 4). BNCP (300 mg) in combination with NCP (50 mg) and filled in detonator No. 10 tetryl (550 mg) also functioned successfully as revealed by damage to the observed witness plate (Table 4).

4 Conclusions

The present work demonstrates the synthesis of dextrinated NHN and dioctyl succinate incorporated BNCP having bulk density of 1.2 and 0.6 g/cm^3, respectively. NHN is sensitive to flash and hot wire and its VOD could be increased to 6900 m/s

Table 4 — Results of functioning of explosive train initiated with NHN based detonator No. 10

Sl No.	Composition charge wt. (mg)	*RDX/TNT charge wt (g)	Initiation method	Observation
1	NHN:CE 350: 550	700	Safety fuse	Explosive train functioned, witness plate damaged
2	NHN:CE 350:550	300	Safety fuse	
3	NHN:CE 500:400	300	LFCN Based General squib	
4	NHN 900	300	Safety fuse	
5	NCP: BNCP:CE 50:300:550	300	Safety fuse	Explosive train functioned, witness plate damaged

* 16 g RDX/Wax perforated booster was assembled in main charge
Number of trials carried out in each experiment: Five
In all the above experiments NHN/BNCP was pressed at 30 MPa and CE was at 10 MPa pressure

(equivalent to that of BNCP) on consolidation to loading density up to 1.72 g/cm^3 at 150 MPa without getting dead pressed. The performance trial results indicated that NHN offers complete replacement for lead styphnate and part replacement of lead azide from ASA composition in detonator No. 27 rendering these devices relatively safer without penalty on performance. NHN alone filled in the stem of detonator No. 10 could be used as an initiator for demolition devices based on high explosive charges. The initiation of BNCP requires the use of high impulse/flash donor compounds, such as NCP and CCP in both the detonator No. 27 and 10. Further work needs to be carried out to establish its application in conventional detonator, despite proven capability as an energetic component of SCB.

Acknowledgement

Authors acknowledge the support received from Shri S R Vadali during the performance trials. They also acknowledge the assistance of Shri P V Kamat and Shri S G Sundaram in determining VOD of NHN and BNCP.

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